PHYSIO MECHANICAL, THERMAL AND BIODEGRADATION STUDIES OF PADDY STRAW POWDER FILLED POLYLACTIC ACID AND POLY (3 HYDROXYBUTYRATE- CO-3- HYDROXYVALERATE) BIOCOMPOSITES

by

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The investigation of the truth is in one way hard, in another easy. An indication of this is found in the fact that no one is able to attain the truth adequately, while, on the other hand, no one fails entirely, but everyone says something true about the nature of all things, and while individually they contribute little or nothing to the truth, by the union of all a considerable amount is amassed – ***Aristotle***

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AA	Acrylic acid
ASTM	American Society for Testing and Materials
C_2H_5OH	Ethanol
$CaCl_2$	Calcium Chloride
CI	Carbonyl Index
CO_2	Carbon Dioxide
DEPC	Diethylpyrocarbonate
DNA	Deoxyribonucleic acid
dNTPS	DeoxynucleotideS
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric
Eb	Elongation at break
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infra Red
HDPE	High Density Polyethylene
KH_2PO_4	Potassium phosphate monobasic
LDPE	Low Density Polyethylene
LLDPE	Linear low-density polyethylene
$MgSO_4$	Magnesium Sulphate
$MgCl_2$	Magnesium Chloride
NaCl	Sodium Cholride
NaOH	Sodium Hydroxide
NCBI	National Centre for Biotechnology Information

Na_2HPO_4-$7H_2O$	Sodium phosphate dibasic heptahydrate
NH_4	Ammonium
NH_4Cl	Ammonium Chloride
PBS	Poly(-butylene succinate)
PCL	Poly(-caprolactone)
PCR	Polymerase Chain Reaction
PDA	Potato Dextrose Agar
PE	Polyethylene
PHA	Polyhydroxyalkanopates
PHB	Poly(3-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PHV	Polyhydroxyvalerate
PLA	Polylactic acid
PLLA	Poly L lactic acid
PP	Polypropylene
PSP	Paddy Straw Powder
SDS	Sodium dodecyl sulfate
SEM	Scanning Electron Microscopy
SSF	Solid State Fermentation
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
UV	Ultraviolet

LIST OF SYMBOLS

%	Percentage
ΔH_f	Heat fusion
ΔH_m	Melt enthalpy
µl	Microliter
µm	Micrometer
°C	Degree Celsius
°C/min	Degree Celsius per minute
cm	Centimetre
g	Gram
g/cm^3	Gram per centimetre cubic
g/l	Gram per litre
g/mol	Gram per mole
GPa	Giga Pascal
h	Hour
kg	Kilogram
kg/m^3	Kilogram per metre cubic
kJ/mol	Kilojoule per mole
kPa	KiloPascal
min	Minute
ml	Millilitre
mm	Millimetre
mm/min	Millimetre per minute
MPa	Mega Pascal

rpm	Revolutions per minutes
s	Second
T	Temperature
T_c	Crystallization Temperature
T_d	Decomposition Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
v/v	Volume per volume
wt %	Weight Percent
w/v	Weight per volume
X_c	Degree of Crystallinity

KAJIAN FISIO MEKANIKAL, TERMAL DAN BIODEGRADASI BIOKOMPOSIT SERBUK JERAMI PADI TERISI ASID POLILAKTIK DAN POLI (3 HIDROSIBUTIRAT- CO-3- HIDROSIVALERAT)

ABSTRAK

Masalah alam sekitar yang berkaitan dengan penggunaan polimer sintetik telah menjurus kepada penggunaan polimer terbiodegradasi dan serat semula jadi untuk menghasilkan satu komposit terdegradasi. Kajian ini dijalankan bagi menghasilkan komposit yang sedemikian dengan penggunaan serbuk jerami padi (PSP) dalam asid polilaktik (PLA) atau poli (3-hidrosibutirat-co-3-hidrosivalerat) (PHBV). Dalam kajian ini, kesan kandungan pengisi, rawatan pengisi semulajadi dan pengadunan dua biopolimer terhadap sifat-sifat mekanikal, fizikal, termal dan ciri-ciri biodegradasi komposit telah dikaji. Pertama sekali, komposit PLA / PSP dan PHBV/PSP yang mengandungi 0-20 wt. % kandungan PSP telah disediakan dengan menggunakan kaedah pencampuran adunan lebur dan kaedah pengacuan mampatan. Penambahan kandungan PSP telah menyebabkan pengurangan kekuatan tegangan bagi kedua-dua komposit. Selain itu, penambahan PSP menunjukkan penurunan kestabilan haba dan telah meningkatkan peratusan penyerapan air kerana sifat hidrofiliknya. Sifat-sifat tegangan, FTIR, SEM dan kehilangan berat oleh sampel yang di tanam di dalam tanah membuktikan aktiviti degradasi untuk suatu tempoh yang telah ditetapkan. Untuk pembandingan, penambahan PSP telah menyebabkan penurunan dalam kekuatan tegangan, tetapi kekuatan tegangan komposit PHBV / PSP adalah lebih rendah berbanding dengan komposit PLA / PSP. Kestabilan haba juga menurun tetapi jauh lebih rendah berbanding dengan komposit PLA / PSP.

Selepas itu kesan pengubahsuaian kimia PSP menggunakan asid akrilik (AA) dan NaOH telah dikaji ke atas sifat mekanik, morfologi dan sifat termal komposit PLA /PSP. Komposit yang dirawat dengan AA dan NaOH mempunyai sifat tegangan yang lebih tinggi berbanding komposit yang tidak dirawat. Pengubahsuaian kimia mempertingkatkan kestabilan termal komposit dirawat. Analisis FTIR menunjukkan pengubahsuaian kimia PSP telah mengurangkan kumpulan hidroksil di dalam PSP. Interaksi antaramuka yang lebih baik antara PSP dan PLA adalah dibuktikan oleh SEM. Untuk kedua-dua jenis pengubahsuaian kimia, asid akrilik menunjukkan kesan yang baik jika dibandingkan dengan NaOH. Seterusnya, pengadunan dua biopolimer PLA dan PHBV dilakukan dalam nisbah 50:50. Kajian adunan PLA / PHBV diperkukuhkan dengan PSP terawat-AA telah dikaji dengan sifat mekanikal, termal, morfologi dan penyerapan air. Kekuatan tegangan adunan PLA / PHBV adalah sedikit lebih rendah berbanding dengan PLA tulen. Penambahan PSP AA dirawat menyebabkan penurunan kekuatan tegangan. Berbanding dengan PLA / PSP (AA-dirawat), komposit PLA / PHBV /PSP menunjukkan sedikit penurunan dalam sifat-sifat tegangan, kestabilan haba dan penyerapan air. Ini mungkin disebabkan oleh antaramuka polimer-polimer yang agak lemah dan ketidakbolehcampuran antara PLA dan PHBV. Akhir sekali, flora kulat yang boleh menguraikan komposit PLA / PSP dan PHBV / PSP telah dikaji dari tanah yang ditanam menggunakan kaedah plat coreng. 5 strain telah dipencilkan iaitu 3 strain dari komposit PLA / PSP (PLA1, PLA2, PLA3) dan 2 strain dari komposit PHBV / PSP (PHBV1 dan PHBV2). Kaedah penjujukan 18s telah digunakan untuk mengenal pasti spesies mikroorganisma yang hadir. Berdasarkan keputusan ini, hanya dua jenis kulat, iaitu *Aspergillus fumigatus* dan *Trichoderma harzianum* yang boleh menguraikan komposit PLA / PSP, manakala bagi komposit PHBVB / PSP , dua jenis kulat juga

iaitu *Aspergillus fumigatus* dan *Aspergillus niveus* terlibat dalam penguraian komposit tersebut.

PHYSIO MECHANICAL, THERMAL AND BIODEGRADATION STUDIES OF PADDY STRAW POWDER FILLED POLYLACTIC ACID AND POLY (3 HYDROXYBUTYRATE- CO-3- HYDROXYVALERATE) BIOCOMPOSITES

ABSTRACT

Environmental problems associated with the use of synthetic polymers have resulted to the utilization of biodegradable polymer and natural fiber for producing fully biodegradable composite. This study has been carried out to produce such composites with the use of paddy straw powder (PSP) in the poly lactic acid (PLA) or poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). In this study, the effect of filler loading, treatment of natural filler and blending of two biopolymers on the mechanical, physical, thermal and biodegradability properties of composites were studied. Firstly, the PLA/PSP and PHBV/PSP composites containing 0-20 wt. % of PSP were prepared by using melt-blended mixing and compression molding method. The addition of PSP had resulted in reduced tensile strength for both of composites. The addition of PSP also showed reduction in thermal stability and has boosted up the water absorption percentages due to their hydrophilic nature. The tensile properties, FTIR, SEM and weight loss of soil buried samples proved the degradation activities over the predetermined time. In terms of comparison tensile strength of PHBV/PSP composites were lower than that of PLA/PSP composites. Thermal stability was also reduced but much lower as compared to PLA/PSP composites. After that the effect of chemical modification of PSP using acrylic acid (AA) and NaOH were studied on the mechanical properties, morphology and thermal

properties of PLA/PSP composites. The treated composites with AA and NaOH have higher tensile properties compared to untreated composites. The chemical modification enhanced the thermal stability of treated composites. The FTIR analysis showed that chemical modification of PSP has reduced the hydroxyl group of PSP. The better interfacial interaction between PSP and PLA was proof by SEM. As compared both of the two types chemical modification, acrylic acid showed a good properties as compared to the sodium hydroxide. Furthermore, blending of two biopolymers which were PLA and PHBV was done in the ratio of 50:50. The PLA/PHBV blends were reinforced with the AA-treated PSP and the mechanical, thermal morphology and water absorption were studied. The tensile strength of the PLA/PHBV blends were slightly lower as compared to the pure PLA. The addition of the AA-treated PSP resulted in reduced tensile strength. As compared to the the PLA/PSP (AA-treated), the PLA/PHBV/PSP composites showed slightly lower tensile properties, thermal stability and water absorption. This may attributed to the relatively weak polymer-polymer interfaces and immiscibility between PLA and PHBV. Lastly, the fungal flora decomposing PLA/PSP and PHBV/PSP composites were investigated from the soil buried of these composites using streak plate method. 5 strains were isolated which are 3 strains from the PLA/PSP composites (PLA1, PLA2, PLA3) and 2 strains from PHBV/PSP composites PHBV1 and PHBV2). 18s sequencing method was applied in order to identify the species of the microorganisms. Based on the results, only two types of fungi, namely the *Aspergillus fumigatus* and *Trichoderma harzianum* were able to degrade the PLA/PSP composite, while for the PHBVB/PSP composite, two types of fungi also, namely the *Aspergillus fumigatus* and *Aspergillus niveus*, were involved.

CHAPTER ONE

INTRODUCTION

1.1 Overview

Many factors, including the decrease in the landfill space, the non-biodegradability of plastic materials in the environment, rapid depletion of petroleum resources and a huge concern regarding ever-increasing environmental pollution, have led scientists to develop materials which can serve as substitutes for petroleum-based plastic materials. A lot of interest has been garnered in this area and huge research is being carried out for evaluating the probability of using biopolymers and other plant-based fibres as substitutes for petroleum polymers or synthetic fibres for their application in the fields of building and construction, automotive and other industries (Pickering et al. 2015; Yan et al. 2014; Siqueira et al. 2010).

There are several advantages in using natural fibres instead of the synthetic fibres as they are cheaper, light weight, have a higher specific strength, and can be processed easily. The natural fibres can be obtained from different plant parts like the leaves, stems and seeds. Some of the most commonly used natural fibres are those obtained from the stem (i.e., bast fibres) of plants like flax, kenaf, hemp, and jute. These are generally used for the reinforcing as they contain a higher tensile strength and better cellulose content (Faruk et al. 2012).

Paddy straw is one of the lignocellulosic filler, which is an agricultural by-product found abundantly in Malaysia, since paddy, in Malaysia, is the first important crop in term of acreage. Paddy straw in Malaysia is presently disposed of mostly by open burning. This results in the release of various pollutants affecting the environment, weather and local communities. Yet, there are several potential uses for

rice straw which can still be explored and developed to benefit Malaysia's rural economy.

In this study, we have defined biocomposites as composites which contain reinforcing fibres along with the polymeric matrix obtained from the renewable resources. Some of the popular commercial biocomposites include the Poly Lactic Acid (PLA), Poly Hydroxy Butyrate (PHB) and the Poly Caprolactone.

1.2 Problem Statements

As already mentioned, due to increasing in the concern regarding the plastic waste disposal and the necessity of a polymer-based material system, there is a huge interest in the development of a biocomposite system using degradable materials and biopolymers.

However, despite the fact that the natural fibres possess good mechanical properties, they also have lower thermal stability and a poor adhesive capacity to the matrix, which can prove challenging. These inherent characteristics of the natural fibres can be improved by surface modifications, which include physical, chemical and biological modifications. Out of all the three techniques, it has been seen that the chemical treatment is the most cost-effective and improves the performance and the fibre-matrix interface. There have been many studies investigating the chemical modification of the fibres; however, they lacked a scientific explanation regarding the causes and the subsequent effect of the modification resulting in microscopic changes in the biocomposite properties.

The widespread use of biopolymers to fill the gap has, however, been hindered by a number of problems, the main concerns being both cost and performance. The good

settings up of the processing parameter need to be consider in order encountering the problem.

In this study, we have tried to successfully develop a novel group of materials which are fully biodegradable polymer (PLA & PHBV) and paddy straw that can be used for the non-structural applications and able to degrade over a period of time. An overview regarding the process capability, compatibility and the biodegradation properties are provided. A development of these biocomposites is seen to be more effective if natural materials are used. This technique was used for developing materials that are more flexible in changing the material properties before their application, reducing costs and making them biodegradable. A surface treatment for modifying the fibre biocompatibility and increasing the number of applications of the natural fibres, without altering the basic properties of the fibres were also applied.

There are very few reports regarding the bacterial degradation of the composites/biocomposites. Also, a lot of researchers are focused on isolating and characterising the microbes which are able to degrade the composites/ biocomposites, however, there are very few studies which have identified and highlighted the role of the microbes on the degradation process.

1.3 Research objectives

The general objective of our research was the development of a biodegradable composite by the incorporation of the natural fibres and a biodegradable polymer. For achieving this objective, several specific objectives have been identified, which are mentioned below.

i. To compare the effect of paddy straw powder (PSP) loading on the mechanical, physical and thermal properties of poly-lactic acid (PLA)/ paddy

straw powder (PSP) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV)/ paddy straw powder (PSP) composites as well as their biodegradability

ii. To investigate the influence of filler treatment (by sodium hydroxide and acrylic acid) on the mechanical, physical and thermal performance of PLA/PSP composite

iii. To determine the effect of blending two biopolymer (PLA and PHBV) with treated PSP on the mechanical, physical and thermal behaviour

iv. To identify through screening and isolation the potential microorganisms that can are able to degrade PLA/PSP and PHBV/PSP composites

1.4 Organization of the thesis

This thesis contains seven chapters with each chapter providing essential information regarding the topic of interest.

- **Chapter 1** introduces the research subject. It includes a brief introduction regarding the research background, contains the problem statement, objectives of the study and the thesis organisation.
- **Chapter 2** describes previously published literature with regards to the topic of research.
- **Chapter 3** comprises important information regarding the material specifications, equipment and the experimental procedures that have been implemented in this study.

- **Chapter 4** contains all the results with respect to the effect of the different loadings of the natural fibres on the PLA and PHBV polymer matrix properties and its biodegradability, have been mentioned here
- **Chapter 5** comprises of the results of the effect of the surface modifications of the natural fibre. Also, in this chapter we have studied the impact of the blended biopolymer on the modified fibre in terms of its biocomposites properties.
- **Chapter 6** contains the result and discussions for the study on the determination of biocomposites degrader microorganisms and its efficiency on the biodegradation of the biocomposites.
- **Chapter 7** contains the final conclusions of the study. It also mentions some suggestions for further research in this area.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

There has been an increasing interest in the development of a material, which while preserving its properties, is also biodegradable. Hence, a literature survey of all the published reports which have studied the relation between natural fibres and the biopolymers are carried out. However, it must be noted that the important issue which is connected to the generation of a natural biocomposite is the presence of the interfacial adhesion between the fibre and the polymeric matrix. Hence, further explanation of the probable chemical surface treatment of the lignocellulosic materials is required. It should be noted that for compensating the limitations of the traditional composite materials, some of the studies have used a common approach, wherein they blended two different biopolymers for attaining diversity in the biocomposite properties. Hence, a lot of reports which used this technique will put forward. Furthermore, the environmental implications of the biocomposites with regards to its biodegradation potential are reviewed. Also, the different microbes that possess the ability to bring about the degradation of these biocomposites will be reviewed. The degradation mechanism used by the microbes for the breakdown of the biopolymers was also investigated. All these parameters would greatly help in understanding the research topic and providing a general overview.

2.2 Environmental Issue and Degradation

The huge environmental problems regarding the wide use of polymers have been a major concern amongst the public as well as the scientific community. One such interest is increasing the amount of litter and solid waste present in the environment,

along with its slow degradation. The increasing production and a low degradation of the commercial polymers have led to its accumulation and increase in environmental pollution.

There have been many diverse polymers which are used as packing materials. They have similar properties of being versatile and having a good performance to cost ratio. Hence, they are largely used in the packaging of different products like cosmetics, pharmaceuticals, food items, detergents and other chemicals. One of the most popular classes of packaging material is the polyethylene (like HDPE, LDPE, and LLDPE) (Dey et al. 2012). However, these polymers are non-degradable, and therefore, can contribute to a huge disposal problem, globally.

As a result, many researchers have begun focusing on the biodegradable materials with regards to their biodegradability and sustainability. Many attempts were made to develop and improve these materials. The primary approach involves the development of the polymeric materials, which are basically biodegradable in nature. The next approach involves the substitution of a constituent present in the existing formulation with a naturally renewable and degradable component. In theory, it is assumed that the biodegradable constituent would be rapidly decomposed by the environmental factors like the moisture, heat, light, chemical condition or any biological activity resulting in the deterioration of the complete polymer (Brandi et al. 1995; Syam & Abdul 2014; Soroudi & Jakubowicz 2013).

In general, the polymer degradation occurs by the cleavage of the side chains of the macromolecules or the main chains by the hydrolysis, oxidation reaction, thermal activation, photolysis, or radiolysis (Rydz et al. 2015).

2.3 Biodegradable Polymer

Biodegradable polymers are defined as the polymers which can undergo the microbial-induced chain scission reaction which leads to oxidation, photo degradation and hydrolysis reactions that alter the properties of the polymer and/or their microstructures during the process of degradation (González et al. 2011). In one other report, it has been said that the biodegradable polymers can undergo their decomposition mainly by the microbial enzymatic reactions, resulting in the production of methane, carbon dioxide, biomass and inorganic compounds (Wei et al. 2015)**.** The general assessment of the biodegradable plastics should be based on the definitions and to what can be defined as the biodegradation of plastics.

Figure 2.1 shows the complete classification of the biodegradable polymers. A majority of biodegradable polymers can be obtained from renewable resources or from biomass (with the exception of the petrochemical family that is origination from the fossils). The biomass family comprises of agro-based polymers that have been developed by the process of fractionation. Furthermore, the microorganism and the biotechnology families comprise of polyesters, which have been developed by the biomass fermentation process, genetically modified plants or by the synthesis from the biomass-based monomers, respectively. Also, the products from the petrochemical family are polyesters but have been synthesised using the petrochemical processes (Avérous & Pollet 2012).

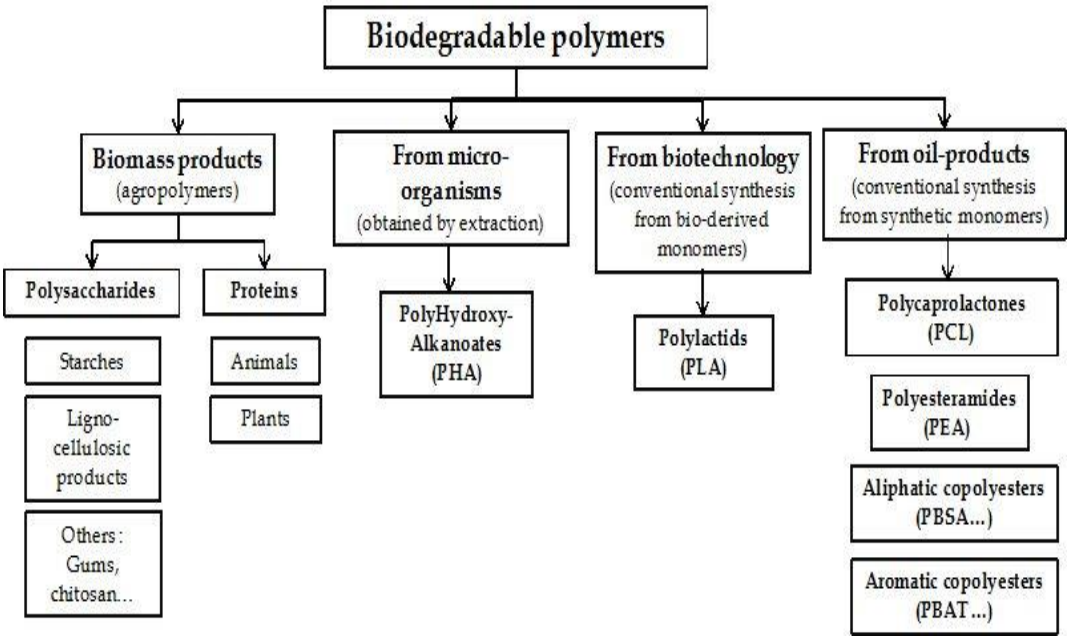

Figure 2.1: Classification of biodegradable polymers (Adapted from (Pickering et al. 2015)

2.3.1 Polylactic Acid (PLA)

PLA is one of the most popular and promising biopolymers which is being produced commercially. Some of its important features include the fact that it is industrially produced from the renewable resources and is compostable in nature. Its mechanical properties can be compared to the Polyethylene Terephthalate (PET) properties, and also, it can be melted using the conventional equipment which is used for the petrochemical-based polymeric materials (Madhavan Nampoothiri et al. 2010). PLA is a type of thermoplastic biopolymer that could be semicrystalline or amorphous, based on the thermal processes it has undergone and the stereochemical structure. It also has a very high mechanical strength along with good barrier properties. It was seen that PLA was initially used for biomedical purposes (Madhavan Nampoothiri et al. 2010; Ding et al. 2015; Jamshidian et al. 2010)

Some physical properties of this polymer are stated here. The density of the amorphous form of PLA is 1.25 g/cm^3, while that for the crystalline Poly (LL-

lactide) or PLLA, is 1.29 g/cm^3. The polylactide molecule is seen to be soluble in alcohols, alkanes and even water. Generally, it is more soluble in acetonitrile, dioxane, dichloromethane and chloroform. PLA is seen to be partially soluble at the room temperature (25°C) in solvents like acetone, benzene, toluene and Tetrahydrofuran (THF) (Jamshidian et al. 2010). Table 2.1 presents selected physical and tensile properties of a typical commercial PLA grade.

Table 2.1: Physical properties of a typical commercial PLA grade (4 % D-lactide) (Madhavan Nampoothiri et al. 2010)

Density at 25 °C (g/cm^3)	1.25
Density of the molten polymer (g/cm^3)	1.07
Glass transition temperature (°C)	55
Melting temperature (°C)	165
Thermal conductivity at 48 °C	0.111 W/(m*°C)
Specific heat capacity at 55 °C	1590 J/(kg*°C)
Tensile strength (MPa)	59
Young's Modulus (GPa)	3.5
Elongation at break (%)	7

The PLA polymer is produced from the lactic acid (2-hydroxy propionic acid) by the fermentation of the renewable resources like sugarcane and corn starch (Chun et al. 2012). The lactic acid is a very simple hydroxyl acid molecule containing an asymmetric carbon atom. It is seen to exist in 2 different optically active configurations, as L (-) lactic and D (+) lactic acid (Figure 2.2) (Gupta & Kumar 2007). Lactic acid is soluble in water, with a 3-carbon chiral structure, occurs naturally and is generally seen in the L (-) configuration. The microbial systems can

produce both the D (+) and L (-) enantiomers of lactic acid. Hence, this molecule can be easily obtained by the fermentation process using proper microorganisms, like the homolactic microbes which are different modified or optimised Lactobacillus strains, which are used for producing the stereoregular L-lactic acid. It has been reported that the lactic acid produced by chemical processes is generally a racemic mixture containing the D- and the L- isomers(Gupta & Kumar 2007; Madhavan Nampoothiri et al. 2010).

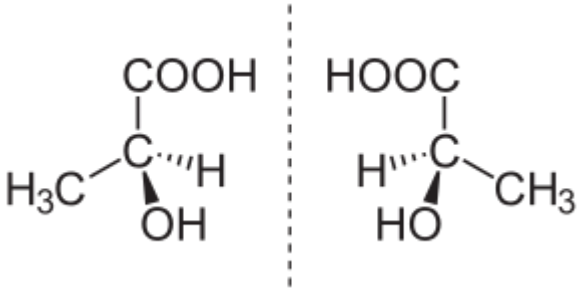

Figure 2.2: Different isomeric forms of lactic acid; left: D- lactic acid and right: L-lactic acid (Adapted from (Madhavan Nampoothiri et al. 2010))

PLA can be produced from the lactic acid molecules using two polymerisation routes, as shown in Figure 2.3. The lactic acid molecules are polymerised using the condensation process to produce a low molecular weight, glass-like and brittle polymer which cannot be used for any purpose unless an external coupling agent is used for increasing its molecular weight as it is difficult to remove water molecules from a very viscous mixture (Gupta & Kumar 2007). The result of the back-biting equilibrium reaction of the resultant low molecular weight molecules is a 6-membered lactide ring (Figure 2.4).

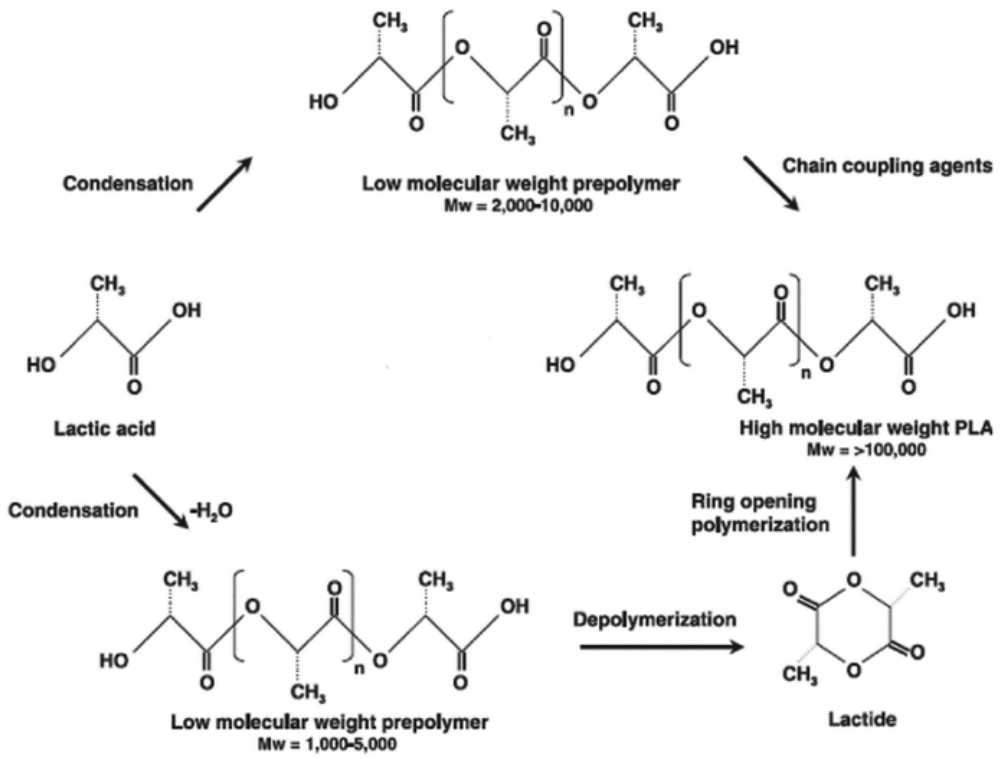

Figure 2.3: Schematic representation of PLA synthesis (Adapted from (Gupta & Kumar 2007)

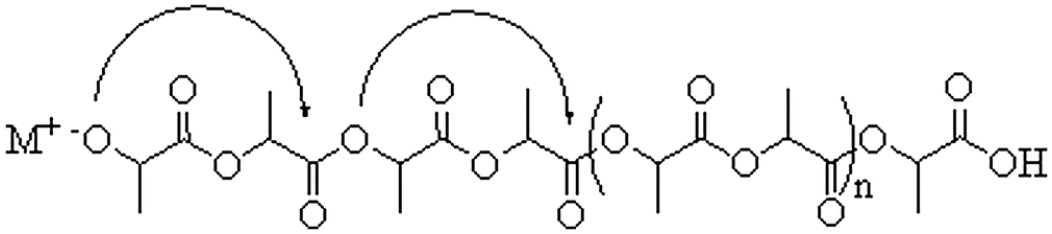

Figure 2.4: Expected formation mechanism of lactide (back-biting mechanism) (Gupta & Kumar 2007)

A controlled depolymerisation of the low molecular weight polymeric compound is carried out to produce the crude lactides that are purified and have to undergo the ring opening polymerisation reaction (in the presence of a catalyst molecule) to produce a high molecular weight polymer molecule. The ring opening polymerisation reaction is divided into two further reactions, involving the cationic

and the anionic ring opening polymerisation reactions. The crude lactides have to be purified to remove the impurities like lactic acid, water and other oligomers that could affect the polymerisation process, resulting in a low molecular weight compound with a higher degree of racemisation. This reaction is solvent-free and has been used by Cargill Dow, who is one of the major producers of PLA, currently. This was the only chemical process which resulted in pure and high molecular weight PLA molecules until a new process was commercialised by Mitsui Toatsu Chemicals, wherein the catalyst and the lactic acid molecules were azeotropically dehydrated in huge assemblies containing a refluxing, boiling, aprotic solvent at very high temperatures and reduced pressure. This led to the production of PLA molecules with an average molecular weight above 300,000 (Gupta & Kumar 2007; Madhavan Nampoothiri et al. 2010; Bajpai et al. 2014).

The PLA is seen to be a thermoplastic, which can be easily processed like the polyolefin plastics such as PolyEthylene (PE) and PolyPropylene (PP). The PLA molecules are processed using traditional processes like the blow moulding, sheet extrusion, injection moulding, thermoforming and the fibre spinning (Bajpai et al. 2014).

This polymer has been used extensively for several years in many biomedical applications like drug delivery, sutures, and orthopaedic implants (Sungyeap Hong 2014). Some of its properties like its ability to be easily processed and good mechanical properties along with its capacity to be biodegraded have made PLA as a very interesting molecule, which can act as a substitute to the non-biodegradable polymers like the PE, PP and PS. In Figure 2.5, some of the applications of the PLA in the packaging industry are depicted.

Figure 2.5: PLA as packaging materials (Avérous & Pollet 2012)

2.3.2 Polyhydroxyalkanoates (PHA)

PHAs belong to the group made up of linear polyesters which are produced by microbes as a main storage source of carbon and energy. This class of compounds has garnered a lot of interest in the scientific community as they are easily biodegradable, sustainable and are environmentally-friendly (Salehizadeh & Van Loosdrecht 2004). Also, PHAs can be made completely biodegradable by the bacterial fermentation process in the culture media (Volova et al. 2010). There are more than 150 monomers reported in the literature. It has been observed that in the case of different monomer constituents, the PHAs show the crystallinity ranging from 30-70% and a melting point value between 50-180°C (Salehizadeh & Van Loosdrecht 2004; Stloukal et al. 2015). PHAs are used in different applications like

electronics, packaging, sensors, energy-related uses, and biomedical (Modi et al. 2015).

The homopolymer of 3-hydroxybutyrate is the compound, Poly(3-hydroxybutyrate) (PHB), Fig. 2.6 (a), which is seen to be a very popular and the best-characterised compound in the polyhydroxyalkanoate family. Some other compounds of this family are presented in Fig.2.6 (b, c). PHB is the linear polyester compound of D (-)-3-hydroxybutyric acid and it was discovered by in 1925 by Lemoigne in the bacterial colonies (Chanprateep 2010). PHB gets accumulated in the intracellular granules in many Gram-positive and Gram-negative bacteria under other nutrient limiting conditions, instead of the carbon source concentration (Bugnicourt et al. 2014). It was seen that the molecular weight of the PHB was different based on the microbial system, growth conditions and the mode of extraction of the molecule, and was seen to vary between 50000 to a million or more. This polymer possessed the important property of biodegradability such as in composts and other environments like the marine waters; therefore, it has attracted a lot of commercial interest.

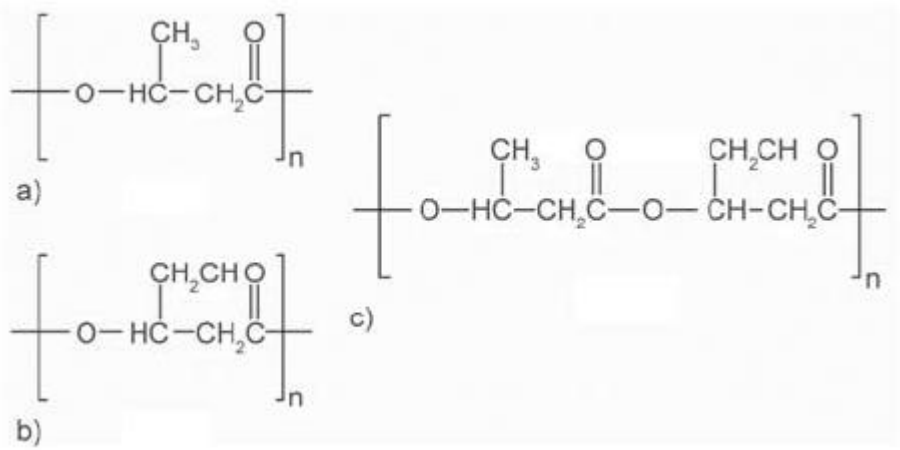

Figure 2.6: Chemical structure of some polyhydroxyalkanoates, a) PH3B, b) PHV, c) PHBV

PHB can be produced by several microbes (e.g., *Ralstonia eutrophus* or *Bacillus megaterium*), which produce this compound under physiological stress. This compound is mostly produced by a pure culture instead of a mixed bacterial population (Volova et al. 2010; Brandi et al. 1995). PHB is basically a product of the carbon assimilation (glucose or starch) and is used by the microbes as an energy storage compound, which can be metabolised if the absence of other energy sources. The microbial biosynthesis of the PHB compound begins by the condensation of two acetyl-CoA molecules, which results in the formation of acetoacetyl-CoA that is then reduced to form hydroxybutyryl-CoA. This molecule is the basic monomer which polymerises to yield PHB. The biologically produced PHB is seen to be a semicrystalline isotactic stereoregular polymer having an R configuration (100%), which helps in its complete biodegradation (Laycock et al. 2014).

There are several applications of PHA due to their novel properties. They are commonly used as packaging films, mostly in containers, bags and paper coatings. It is used in many other applications as a commercial commodity plastic material like utensils, razors, diapers, female hygiene products, or as cosmetic containers—cups or shampoo bottles. Furthermore, PHA can also be used as a stereoregular compound that acts as a chiral precursor for chemically synthesis of optically active compounds (Chanprateep 2010). These compounds are used in the form of biodegradable carriers for a long-term dosage of the medicines, drugs, hormones, herbicides and insecticides. Additionally, PHA is used as an osteosynthetic material in stimulating the bone growth due to its piezoelectric properties, in the surgical sutures, bone plates, and in blood vessel replacements. Despite these uses, because of its slow degradation rate and high hydraulic stability in the sterile tissues, the medical and the

pharmaceutical applications of this compound are limited (Khanna & Srivastava 2005). PHA is also used for synthesising chiral compounds (i.e., enantiomerically pure compounds) and as raw materials for paint production.

The important characteristic feature of PHA which distinguishes it from other petroleum-based plastic materials is its biodegradability. The PHA can be easily degraded after they are exposed to compost, soil or marine sediments. The biodegradation is seen to depend on various factors like the environmental microbial activity, along with the surface area exposed, temperature, pH, moisture, molecular weight etc. (Li et al. 2015b). Similarly, the nature of monomer units in the compound also affects its biodegradability. It has been observed that the copolymers having PHB monomer units are more rapidly degraded as compared to either the PHB or the 3HB-co-3HV copolymers. Microbes secrete enzymes which help in degrading the polymer into the molecular building blocks, known as hydroxyl acids that are then used as a source of carbon and energy to support the growth of the microbes. The main enzyme that brings about the PHB and its oligomer degradation is the PHB depolymerase.

2.4 Natural Fibers as Reinforcement in Biocomposites

Based on the origin source, natural fibres are obtained from the plants, animals or from minerals. The classification of natural fibres has been shown in Figure 2.7.

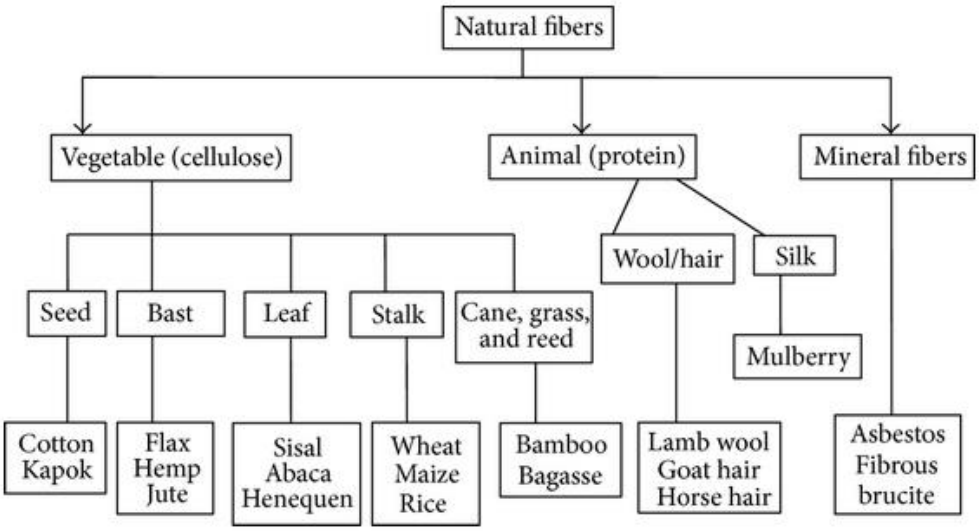

Figure 2.7: Classification of natural fiber (Faruk et al. 2012)

Biopolymer composite properties can be strengthened by incorporating reinforcements like natural fibres, thereby making it better for many engineering applications. Hence, over a period of time, the need for the natural fibre-reinforced composites has increased significantly for many commercial applications (Faruk et al. 2012).

There have been many reports which have highlighted the increasing significance of these composites. The different natural fibres used for reinforcing the polymeric matrices are listed in Table 2.2.

Table 2.2: Recent reported worked on natural fibers and polymer composites

Fiber	Matrix	References
Bamboo	Polylactic acid	(Wang et al. 2014)
Coir	Poly lactic acid	(Dong et al. 2014)
Sugarcanne	Polyhydroxy-3-butyrate valerate	(Salles et al. 2015)
Kenaf	Polylactic acid	(Hidayat & Tachibana 2012)
Rice & Wheat husk		(Phuong et al. 2014)
Bamboo, grass & coconut	Polylactic acid	(Sujaritjun et al. 2013)
Rice Hull	Polyhdroxybutyrate	(Alberti et al. 2014)
Wood & Kenaf	Polyhdroxybutyrate	(Kuciel & Liber-Kneć 2011)

Also, due to the huge environmental issues, many researchers worldwide are beginning to show an increasing interest in investigating the complete potential of the natural fibres as the reinforcing materials of the biopolymer composites and with their different applications.

Natural fibres have more advantages as compared to carbon fibres and glass; therefore, they help in fulfilling the composite requirements. These natural fibres can be used in the polymer composites without any effect on their rigidity (Faruk et al. 2012).

Natural fibres possess a very intricate structure consisting of a primary cell wall along with 3 secondary walls. The structure of a natural fibre has been shown in Figure 2.8. Every cell wall is made up of three important components, i.e., cellulose, hemicellulose and the lignin molecules. The lignin- hemicellulose act as the matrix, while the microfibril (consisting of the cellulose) act as the fibres (Pickering et al. 2015). In the plant fibres, cellulose is a natural polymer wherein every repeating unit is made up of 3 hydroxyl groups. The cellulose molecule is very resistant to strong

alkali, hydrolysis and some oxidising agents; however, it is partially degraded on exposure to strong chemicals and chemical treatments.

Hemicellulose is a polysaccharide molecule having a low molecular weight. This molecule acts as the cementing molecule between the cellulosic microfibrils and forms the main structural unit of the cell. Hemicellulose is hydrophilic in nature and is easily hydrolysed even by the dilute acids and base solutions. On the other hand, lignin is a very complex hydrocarbon polymer which provides rigidity to the plants and helps in transporting water. This molecule appear hydrophobic in nature, is seen to resist the acid hydrolysis and many microbial attacks. It is solubilised in the hot alkaline solutions, is easily oxidised and is easily condensed using phenol (Azwa et al. 2013).

Table 2.3 lists some of the chemical compositions of the commonly used cellulosic and the lignocellulosic fibres. As already mentioned, the natural fibres are mainly made up of the cellulose, lignin and the hemicellulose molecules, with pigments, pectins and some extracts being present in small amounts. Natural fibre is also called cellulosic or the lignocellulosic fibre because every fibre is mainly A composite where rigid cellulose microfibrils are seen to be embedded in a soft matrix which is mainly composed of hemicellulose and lignin molecules (Luduena et al. 2012).

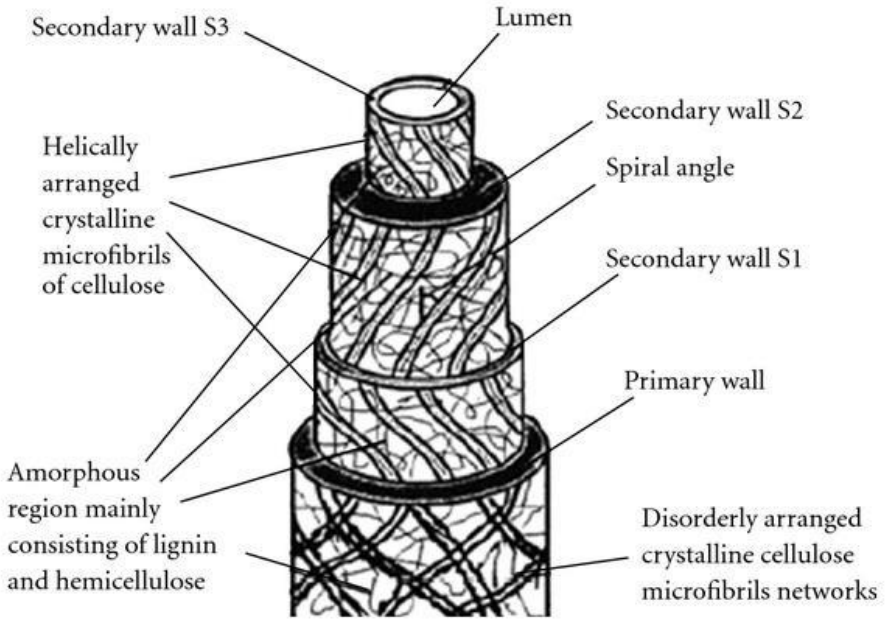

Figure 2.8: Structural of natural fiber cell (Adapted from (Azwa et al. 2013)).

Table 2.3: Chemical compositions of various natural fibers (Faruk et al. 2012)

Fiber	Cellulose (wt. %)	Hemicellulose (wt. %)	Lignin (wt. %)	Waxes (wt. %)
Baggase	55.2	16.8	25.3	-
Bamboo	26-43	30	21-31	-
Flax	71	18.6-20.6	2.2	1.5
Kenaf	72	20.3	9	-
Jute	61-71	14-20	12-13	0.5
Hemp	68	15	10	0.8
Ramie	68.6-76.2	13-16	0.-0.7	-
Abaca	56-63	20-25	1-9	3
Sisal	65	12	9.9	2
Coir	32-43	0.15-0.25	40-45	-
Oil Palm	65	-	29	-
Pineapple	81	-	12.7	-
Curaua	73.6	9.9	7.5	-
Wheat straw	38-45	15-31	12-20	-
Rice Husk	35-45	19-25	20	14-17
Rice straw	41-57	33	8-19	8-38

Other than the chemical composition, the cellulosic fibre properties are also influenced by the different morphological characteristics like the microfibril angle, internal fibre structure, dimension and the cellular defects (Majeed et al. 2013).

Researchers believe that the microfibrillar angles can affect the mechanical properties of the fibres. Also, it is seen that natural fibres that are having a high cellulose content, a higher degree of cellulose polymerisation, longer cell length and a low microfibrillar angle, display better mechanical strength (Azwa et al. 2013).

Table 2.4 illustrates the mechanical and physical properties of natural fibers as available in the literature. The natural fibres show different properties in different studies, as different fibres were used, the moisture conditions varied in every study and furthermore, the testing procedures were also different (Faruk et al. 2012).

Table 2.4: Mechanical and physical properties of various natural fibers (Majeed et al. 2013)

Fiber	**Tensile Strength (MPa)**	**Young's Modulus (GPa)**	**Elongation at break (%)**	**Density (g/cm^3)**
Abaca	400-980	6.2-20	1.0-20	1.5
Alfa	35	22	5.8	0.89
Baggasse	222-290	17	1.1	1.25
Bamboo	140-800	11-32	2.5-3.7	0.6-1.1
Banana	500	12	1.5-9	1.35
Coconut	131-175	4-13	-	-
Coir	95-230	2.8-6	15-51.4	1.15-1.46
Flax	343-2000	27.6-103	1.2-3.3	1.4-1.5
Hemp	270-900	23.5-90	1-3.5	1.4-1.5
Henequen	430-570	10.1-16.3	3.7-5.9	1.2
Jute	320-800	8-78	1-1.8	1.3-1.49
Kenaf	223-920	14.5-53	1.5-2.7	1.4
Piassava	134-143	1.07-4.59	7.8-21.9	1.4
Ramie	560	24.5	2.5	1.5
Sisal	363-700	9.0-38	2.0-7.0	1.33-1.5

The use of the natural fibres as the reinforcing materials in the composites is still being studied. This is due to the fact that there are many challenges related to the application of the fibres as reinforcing materials. Some of these are as follows; there is an incompatibility between the polymeric matrices and the natural fibres, controlled processing temperature and a poor moisture resistance. These limitations

are due to the presence of the hydroxyl and other polar groups in the fibre, which contributes towards their hydrophilicity (Sujaritjun et al. 2013; Lomelí-Ramírez et al. 2014). Hence, if these issues are addressed, the biocomposite performance could be greatly enhanced and there would be an increase in the application of these materials. Many studies have carried out fibre treatment for improving the compatibility between the polymer and the natural fibres (Husseinsyah et al. 2011; Obasi et al. 2014; Sujaritjun et al. 2013; Yeo et al. 2015).

Due to the above-mentioned conditions, paddy straw has begun gaining the attention of the researchers, as this fibre is found in abundance and can be used for many purposes (Buzarovska et al. 2008). The biocomposites reinforced with the paddy straw powder need to be studied further. This fibre has been successfully incorporated in many applications. In this work, the characteristics of the paddy straw fibre as reinforcing materials in the biopolymer composites will be investigated, and the details will be presented in Section 2.4.1.

2.4.1 Paddy Straw

In Asian countries, paddy / rice is a very important agricultural crop. With regards to the production, paddy is only behind wheat and corn, globally (Buzarovska et al. 2008). Due to its large usage, paddy straw is one of the most important residues that get generated in huge amounts in the Asian countries. Each kilogram of the harvested grain results in 1-1.5 kg of rice straw. A large amount of the rice straw is burnt in the rice fields. However, this burning of the rice straw results in huge air pollution and release of particulate matter into the atmosphere. Two major residues are generated from the rice production, i.e., rice straw and rice husk. The rice straw refers to the residue that is left after the grain has been harvested

and it contains the stem, leaves and the spikelets. Traditionally, rice straw is used as an animal feed and a feedstock in the organic fertiliser and the paper industries. The rice straw is disposed by ploughing it in the soil or is burnt (Abraham et al. 2016).

This straw is collected and is baled after it has dried and the moisture content has decreased below 25%, which is within 3-4 days of the harvest but mainly depends on the climatic conditions (Nemr & Shazly 2015). After baling, the straw looks like flat fibres (approximate dimensions: 20-60 cm long and 0.5 cm wide). Fig. 2.9 (a) shows a photograph of the paddy straw, which has been taken from the cylindrical bale, after 4 months of harvest, whereas the Fig. 2.9 (b) shows a cross section of the paddy plant. The paddy straw is generally used as a reinforcing material in the polymer composites as it is seen to be abundantly present as the agricultural by-product of the rice production.

The lignocellulosic fibres are used for reinforcing the thermoplastic and the thermosetting resins from the petroleum or the natural feedstock. Similar to conventional composites, the natural fibres present in the bio-composites act as the reinforcing materials, which help in improving the performance of the composite materials. This leads to an increase in the mechanical properties like stiffness and strength and a decrease in weight, which improves the efficiency of the composites.